

Determination of very toxic metal – Cadmium in natural water samples

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ARTICLE INFO

Article history:

Accepted 16 March 2009

Available online 29 September 2009

Keywords:

Potentiometric stripping analysis

Cadmium

Water

ABSTRACT

A potentiometric stripping method for a direct measurement of cadmium in various natural water samples using a Stripping analyzer M1 (designed and manufactured in Serbia) unit has been developed. In order to ascertain optimum conditions for the determination of the effect of the mercury time electrodeposition, the electrolysis potential and the solution stirring rate of the cadmium analytical signal have been examined. Linearity of the cadmium analytical signal was achieved within the wide range of the mass concentrations, from 1 µg/L to 15 µg/L. A detection limit of 0.10 µg/L was obtained, with a reproducibility of 3.55% expressed as the coefficient of variation. The accuracy of the method was confirmed by parallel analyses by flameless atomic absorption spectrophotometry as the reference method.

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1. Introduction

Development of civilization is accompanied by an enhancement of environmental contamination by many metals, among which cadmium is one of the most dangerous. Cadmium is still an important industrial metal. The use of cadmium products has expanded in recent years at a rate of 5 to 10% annually, and the potential for further growth is very high [1]. Cadmium is used primarily for electroplating other metals or alloys to protect them against corrosion. It is employed extensively in the production of low-melting-point alloys, solders, and low-cadmium copper. Cadmium is also used in the manufacture of stearate stabilizers for plastics, notably polyvinyl chloride, and pigments [2,3].

Small amounts of cadmium enter the environment from the natural weathering of minerals, forest fires, and volcanic emissions, but most is released by human activities such as mining and smelting operations, fuel combustion, disposal of metal-containing products, and application of phosphate fertilizer or sewage sludges [2,3]. These cadmium pollutants may be transported from a hundred to a few thousand kilometers and have a typical atmospheric residence time of about 1–10 days before deposition occurs [4]. Larger cadmium-containing particles from smelters and other pollutant sources are also removed from the atmosphere by gravitational settling, with substantial deposition in areas downwind of the pollutant source. Cadmium-containing particulates may dissolve in atmospheric water droplets and removed from air by wet deposition [4].

Cadmium is more mobile in aquatic environments than most other heavy metals (e.g., lead). Cadmium in soils may leach into water. Cadmium-containing soil particles may also be entrained into the air

or eroded into water, resulting dispersion of cadmium into these media [5]. Cadmium concentration in water is inversely related to the pH and the concentration of organic material in the water [5]. Cadmium is taken up and retained by aquatic and terrestrial plants and is concentrated in the liver and kidney of animals that eat the plants, and enters the food chain for humans [2].

Human exposure to cadmium can result from consumption of food, drinking water, or incidental ingestion of soil or dust contaminated with cadmium; from inhalation of cadmium-containing particles from ambient air; from inhalation of cigarette smoke, which contains cadmium taken up by tobacco; or from working in an occupation involving exposure to cadmium fumes and dust [6].

Cadmium is considered as one of the most dangerous occupational and environmental poisons. It is presumed that the respective amount of this metal in the organism is undesirable. The basis of cadmium toxicity is its negative influence on enzymatic systems of cells, owing to substitution of other metal ions (mainly Zn^{2+} and Cu^{2+}) in metalloenzymes and its very strong affinity to biological structures containing –SH groups [7–9]. Excessive Cd exposure may give rise to renal, pulmonary, hepatic, skeletal, reproductive effects and cancer. The major effects of this metal poisoning are experienced in the lungs, kidneys and bones [10,11]. Obviously, the monitoring of cadmium level at trace level in different environment matrices that is directly related with human health has a high importance. The World Health Organization (WHO) reported tolerable weekly intakes of cadmium as 0.007 mg/kg body weight, for all human groups [12]. Briefly, it is seen that this metal can dangerously affect human health even at ultra trace concentrations.

The determination of cadmium in natural waters is increasingly growing due to the knowledge of its extreme toxicity for human even at very low levels. As a result, the maximum allowable Cd in drinking water was restricted to 5 and 20 ng/mL, by international regulations on

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water quality including WHO, EU, EPA and other authorities [12–14]. Cadmium concentrations in natural water samples were reported in the range of 0.06–4.3 µg/L for tap water, 0.12–4.7 µg/L for river and 0.02–58.6 µg/L for sea water [15–17].

Analytical methods used for measuring concentrations of cadmium in water samples include atomic absorption spectrometry (AAS), neutron-activation analysis (NAA), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and electrochemical stripping analysis (ESA). The success as well as the frequency of the above-mentioned techniques is different; they both depend on the detection limit, selectivity and reproducibility of the given technique, the rapidity and simplicity of the method as well as the price of the device and its exploitation [18–20].

The electrochemical stripping analysis (ESA) has the greatest sensitivity (10^{-11} mol/L) just after the neutron-activation analysis (10^{-21} mol/L). Besides, the cost of its application and exploitation is much lower than with the other above-mentioned techniques while the procedure for carrying out the analysis is relatively simple and fast.

The aim of the paper is to define the method for determining the cadmium in the natural water samples by applying the potentiometric stripping analysis (PSA) with oxygen as an oxidant [21,22].

2. Experimental

2.1. Chemicals

Hydrochloric acid (suprapur grade), standard solution of cadmium (1 g/L, *Titrisol*), and standard solution of mercury (1 g/L, *Titrisol*) were purchased from Merck (Darmstadt, Germany) and have been used as received. Working solutions were prepared by dilution of standard solution with doubly distilled water.

All containers, vessels and cells were washed with nitric acid (1:1) and doubly distilled water before used.

2.2. Apparatus and instrumental conditions

All the analyses were performed by using commercially available computerized Stripping analyzer M1 (Faculty of Technology, Novi Sad and Elektrouniverzal, Leskovac, Serbia). The analyzer has a program for automatic qualitative and quantitative determination, involving the calculation of element contents. The instrument can be programmed to give deposition potentials between -2 and 2 V and a constant current for the electrolysis or stripping step between -50 and 50 µA, with the parameter setting accuracies $\Delta E < 2$ mV and $\Delta I < 0.2$ µA. The time lapse between two consecutive equivalence points is taken as a measure of the sample concentration of the particular analyte dissolved in this interval. The dissolution time measuring accuracy is $\Delta t = 50$ ms. Qualitative identification is based on the element dissolution potentials. The potential signal measuring resolution is $E = 2$ mV [23].

The electrochemical cell consists of mechanical Teflon stirrer (1000–6000 r.p.m.), an electromagnetic valve, electrodes and the process vessel.

A glassy carbon (SIGRADUR-G) working electrode of a total surface area of 7.07 mm^2 was pressed into the Teflon tube (outer diameter 8 mm) at an elevated temperature. An Ag/AgCl, KCl (3.5 mol/L) electrode was used as the reference and a platinum wire as the counter electrode.

A glassy carbon disc working electrode was used as an inert support for the mercury film. Before electrode formation, the glassy carbon surface was swept with filter paper first soaked with acetone and then with doubly distilled water. The mercury film was formed electrolytically from a solution containing 100 mg/L mercury(II)-ions and 0.02 mol/L hydrochloric acid, at a constant current of 50 µA for

240 s. Once deposited, the mercury film could be used for 25–30 analyses.

Flameless atomic absorption spectrophotometry (FAAS) measurements were carried out with Perkin Elmer 1100 AAS spectrophotometer.

For the cadmium determination by FAAS the following five-step procedure was adopted:

1. Step — drying of sample for 30 s at 150°C with temperature ramp up time of 10 s
2. Step — sample mineralization for 5 s at 700°C with temperature ramp up time of 5 s
3. Step — sample atomization at 1600°C (instantly reached) with integration time of 3 s
4. Step — cuvette cleaning at 2500°C for 1 s with temperature ramp up time of 1 s
5. Step — cooling of the cuvette for 10 s at 20°C with temperature ramp down time of 5 s.

Hollow cathode lamp with 228.80 nm wavelengths was used as a radiation source. The argon flow rate through the graphite cuvette was $300 \text{ cm}^3/\text{min}$. Sample volume for all analyses was 20 mm^3 .

2.3. Sample preparation

The various natural water samples (sea, river, mineral and tap water) are acidulated with HCl up to pH ~ 2 and directly tested using PSA method of analysis.

3. Results and discussion

3.1. The PSA of cadmium

In order to optimize the PSA determination of cadmium the effect of mercury time electrodeposition, the electrolysis potential, and the solution stirring rate of the cadmium analytic signal were investigated. After the optimization of the determination conditions, both the linearity and the reproducibility of the analytical signal were defined.

The oxygen as an oxidant was applied to eliminate the time consuming deaeration step and prevention of the sample contamination by the inert gas used for deaeration as well as by chemical that must be added as oxidant.

3.2. The mercury time electrodeposition effect on the cadmium PSA

The mercury film on the glassy carbon as an inert support was formed electrolytically from the solution containing 100 mg/L mercury (II) and 0.02 mol/L hydrochloric acid, at the constant current of 50 µA and during 120 to 360 s. Effect of the mercury time electrodeposition was investigated on the basis of reproducibility of the analytical signal upon the cadmium PSA of the mass concentrations of 5 µg/L and 10 µg/L at the electrolysis time of 900 s and 300 s, respectively and with potential on the working electrode of -1.067 V against Ag/AgCl, KCl (3.5 mol/L) electrode. Dependence of the reproducibility of the cadmium PSA expressed through the oxidation time (t_{ox}) and coefficient of variation ($C_V = \text{Standard deviation} / \text{mean value} \cdot 100$) of the mercury time deposition ($t_{dep \text{ Hg}}$) are presented in Table 1.

Regarding results of the investigations it can be said that the best results were acquired at the mercury time deposition of 240 s, with reproducibility expressed through the coefficient of variation (C_V) of 0.00 and 4.45% (the cadmium concentration of 5 µg/L and 10 µg/L, respectively).

3.3. The solution stirring rate effect on the cadmium PSA

The solution stirring rate (that is, of a Teflon stick stirrer revolution) was examined at the values of 1000, 2000, 4000 and 5000 r.p.m.

Table 1

Dependence of the reproducibility of the cadmium PSA expressed through the oxidation time (t_{ox}) and coefficient of variation (C_V) of the mercury time deposition ($t_{dep\ Hg}$).

$t_{dep\ Hg}$ (s)	Cd concentration			
	5 $\mu\text{g/L}$		10 $\mu\text{g/L}$	
	t_{ox}^a (s)	C_V (%)	t_{ox}^a (s)	C_V (%)
120	0.26 ± 0.012	4.85	0.32 ± 0.021	6.65
180	0.28 ± 0.013	4.60	0.30 ± 0.016	5.33
240	0.32 ± 0.000	0.00	0.34 ± 0.015	4.45
300	0.28 ± 0.000	0.00	0.34 ± 0.028	8.32
360	0.32 ± 0.048	1.50	0.31 ± 0.028	9.15

^a Values represent mean oxidation time of five replicates.

At the solution stirring rate of 6000 r.p.m. the investigation cannot be carried out because of peelings mercury layer from the surface of the glassy carbon electrode.

The effect of the solution stirring rate on the cadmium analytical signal (t_{ox}) for the cadmium content of 5 $\mu\text{g/L}$; t_{el} = 900 s and for cadmium content of 10 $\mu\text{g/L}$; t_{el} = 300 s are presented in Table 2. In view of the fact that the major and the most reproducibility values of the analytical signals were obtained at the solution stirring rate of 4000 r.p.m., this solution rate was chosen as the optimal for further determinations.

3.4. The electrolysis potential effect on the cadmium PSA

To define the optimal electrolysis potential, the potentials from -0.911 V to -1.160 V were examined against the Ag/AgCl, KCl (3.5 mol/L) reference electrode at the electrolysis time of 900 s for the solution with concentration of 5 $\mu\text{g/L}$ and 300 s for the concentration of 10 $\mu\text{g/L}$ and with the stirring rate of 4000 r.p.m.

These investigations were carried out in two ways.

In the first part the cadmium contents were determined on the formed thin-layered deposited mercury in the potential range from -0.911 V to -1.160 V then the mercury was removed and again formed in the same solution, in the same range of the potentials and for the same electrolysis time. The investigations at these conditions at five replicates were done.

In the second part of the investigations five analyses were done at the mercury deposited layer at one potential value (for example -0.911 V) then the mercury layer was removed and deposited again for the next potential values.

The effects of the electrolysis potential on the cadmium analytical signal (t_{ox}) for the cadmium content of 5 $\mu\text{g/L}$; t_{el} = 900 s and for cadmium content of 10 $\mu\text{g/L}$; t_{el} = 300 s on the reproducibility of the determinations expressed through the coefficient of variation (C_V) are presented in Tables 3 and 4.

In Table 3, we can see that on the same mercury layer the cadmium analytical signal has good arising linearity of the electrolysis potential.

Table 2

The reproducibility of the analytical signals expressed through the oxidation time (t_{ox}) and coefficient of variation (C_V) of the solution stirring rate.

n (r.p.m.)	Cd concentration			
	5 $\mu\text{g/L}$		10 $\mu\text{g/L}$	
	t_{ox}^a (s)	C_V (%)	t_{ox}^a (s)	C_V (%)
1000	0.27 ± 0.011	4.25	0.30 ± 0.026	8.85
2000	0.28 ± 0.016	5.60	0.33 ± 0.020	6.23
4000	0.34 ± 0.008	2.34	0.36 ± 0.013	3.58
5000	0.37 ± 0.029	7.86	0.42 ± 0.045	10.72

^a Values represent mean oxidation time of five replicates.

Table 3

The reproducibility of the analytical signals expressed through the oxidation time (t_{ox}) and coefficient of variation (C_V) of the electrolysis potential for the determinations on the same thin-layered mercury.

E (V)	Cd concentration			
	5 $\mu\text{g/L}$		10 $\mu\text{g/L}$	
	t_{ox}^a (s)	C_V (%)	t_{ox}^a (s)	C_V (%)
-0.911	0.23 ± 0.009	4.16	0.25 ± 0.020	8.20
-0.973	0.27 ± 0.010	3.76	0.23 ± 0.011	4.66
-1.020	0.29 ± 0.007	2.55	0.25 ± 0.012	4.88
-1.067	0.34 ± 0.00	0.00	0.30 ± 0.003	1.15
-1.112	0.36 ± 0.011	3.20	0.31 ± 0.015	5.00
-1.160	0.42 ± 0.027	6.58	0.32 ± 0.018	5.68

^a Values represent mean oxidation time of five replicates.

But the same dependencies investigated on the different layers were disorderly with increasing or decreasing values (Table 4). From this investigation (from the shape and character of functional dependencies) it can be concluded that analysis of the same series is much better to perform on the same mercury layer. We can point out that at negative values of the electrolysis potentials reproducibility is decreasing because of the hydrogen evolution on the working electrode, so for the optimum potential value -1.067 V was chosen.

3.5. The linearity of analytical signal effect on the cadmium PSA

The linearity of the analytical signal effect on the cadmium PSA was examined for the mass concentration of 1–15 $\mu\text{g/L}$ on the optimum conditions already accepted (the electrolysis potential of -1.067 V ; the electrolysis time of 900 s and the solution stirring rate of 4000 r.p.m.). That was performed on the following way: on the deposited mercury layer cadmium of 1 $\mu\text{g/L}$ was analyzed, then the electrode was rinsed with doubly distilled water, drained by the paper, then the same procedure was repeated with new cadmium contents of 3, 5, ..., 15 $\mu\text{g/L}$ respectively. After the first series mercury layer was peeled and the new mercury layer was deposited for the new series determinations in the same concentrations range. The linearity was examined at the five series. In each linear functions ($\tau_{ox} = a + b \cdot C_{Cd}$) parameters a , b and correlation coefficient (r) were calculated. In Fig. 1, mean values for a , b and r are presented.

$$\tau_{ox} = 0.0712 + 0.03905 \cdot C_{Cd}; r = 0.99821.$$

Regarding a high value of the correlation coefficient ($r > 0.990$) it is obvious that there is a very good linearity of the analytical signal within the examined cadmium concentration range.

3.6. Detection limit

A detection limit of the PSA of cadmium is 0.10 $\mu\text{g/L}$, for an electrolysis time of 900 s, at an electrolysis potential of -1.067 V ,

Table 4

The reproducibility of the analytical signals expressed through the oxidation time (t_{ox}) and coefficient of variation (C_V) of the electrolysis potential for the determinations on the different thin-layered mercury.

E (V)	Cd concentration			
	5 $\mu\text{g/L}$		10 $\mu\text{g/L}$	
	t_{ox}^a (s)	C_V (%)	t_{ox}^a (s)	C_V (%)
-0.911	0.24 ± 0.013	5.63	0.22 ± 0.017	7.75
-0.973	0.24 ± 0.025	3.25	0.26 ± 0.010	5.66
-1.020	0.30 ± 0.016	5.58	0.25 ± 0.015	4.88
-1.067	0.32 ± 0.008	2.50	0.34 ± 0.011	3.15
-1.112	0.32 ± 0.013	4.20	0.35 ± 0.026	7.55
-1.160	0.36 ± 0.027	7.58	0.36 ± 0.031	8.58

^a Values represent mean oxidation time of five replicates.

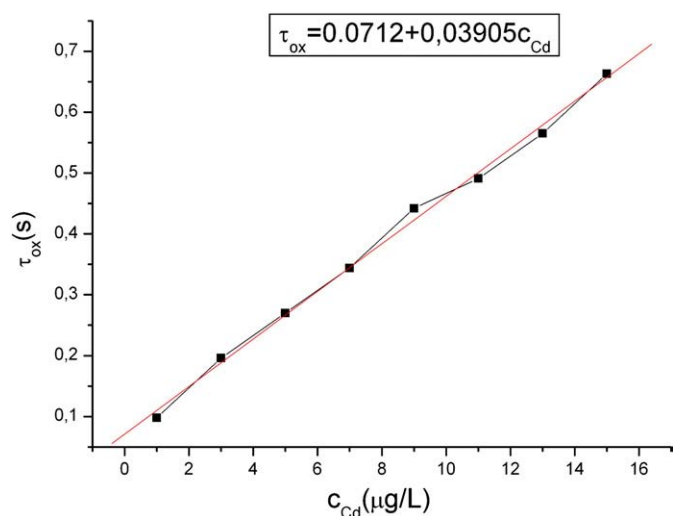


Fig. 1. The linearity of the cadmium analytical signal (τ_{ox}) expressed through mean values of the parameters a , b and the correlation coefficient (r).

with a stirring rate of 4000 r.p.m. Good reproducibility was obtained with 3.55%.

3.7. The PSA of cadmium in natural water samples

On the basis of the above examinations the method for determining the cadmium in the various natural water samples by the potentiometric stripping analysis (PSA) with oxygen as an oxidizer was defined. Defined method considering samples analysis (sea, river, mineral and tap water) on the thin-layered mercury electrode with the electrodeposited mercury depth of 130 nm on the glassy carbon as inert support formed at a constant current of 50 μ A, at the electrodeposition time of 240 s; at the electrolysis potential of -1.067 V against Ag/AgCl, KCl (3.5 mol/L) electrode, during 900 s and the stirring rate rapidity of 4000 r.p.m.

The cadmium concentration was calculated according to the following calibration curve:

$$C_{Cd} = \tau_{ox} - 0.00244 / 0.11463; (r = 0.9986)$$

which was obtained for the concentration range from 0.1 to 1 μ g/L under above-mentioned conditions of analysis.

The calibration curve was also obtained in the concentration range from 2 to 14 μ g/L Cd. The obtained graph was linear in the concentration range described above, and the equation of the curve was follow:

$$C_{Cd} = \tau_{ox} - 0.09143 / 0.04411; (r = 0.9989).$$

The results obtained by the PSA method and the results of the reference FAAS method are given in Table 5, together with the results of the relative deviation of the two methods and the coefficients of variation.

The results of the comparative analysis showed a very good agreement between the PSA and the FAAS methods. The best results agreement was achieved with the samples with micro cadmium contents as achieved, thanks to the great sensitivity of the given method in analyzing the cadmium in the water samples.

On the basis of the values of the coefficient of variation, it can be concluded that it is possible to apply the calibration curve method for obtaining more reproducible values than by the standard addition method where the deviations are somewhat greater. Hence, the calibration curve method is proposed as the standard method for the determination of cadmium in the various natural water samples.

4. Conclusion

The results given in this paper show that the PSA with oxygen as an oxidizer can be successfully applied for determining the residuals of the cadmium in the natural water samples (sea, river, mineral and tap water).

The selective, sensitive and reproductive method for the cadmium PSA for the given purposes was defined. A glassy carbon electrode with mercury depth of 130 nm electrodeposited at constant current of 50 μ A, during 240 s has been used as working electrode. The analyses have been carried out at electrolysis potential of -1.067 V (Ag/AgCl, 3.5 mol/L, KCl), during 900 s and the stirring rate rapidity of 4000 r.p.m. All results were confirmed by parallel FAAS comparative analysis.

Acknowledgment

These results are part of the projects 145072 and 18206, partly financially supported by the Republic of Serbia Ministry of Science and Environmental Protection.

Table 5

Cadmium contents in the water samples determined by PSA and FAAS methods.

Source of water	Potentiometric stripping analysis						FAAS	
	Calibration curve method			Standard addition method				
	Pb (μ g/L)	δ^* (%)	C_V (%)	Pb (μ g/L)	δ^* (%)	C_V (%)	Pb (μ g/L)	C_V (%)
Tap 1	0.12 \pm 0.009	9.09	7.50	0.13 \pm 0.010	18.18	7.69	0.11 \pm 0.008	7.27
Tap 2	0.25 \pm 0.021	8.70	8.40	0.24 \pm 0.021	4.35	8.75	0.23 \pm 0.015	6.52
Tap 3	0.36 \pm 0.030	– 5.26	8.33	0.37 \pm 0.031	– 2.63	8.38	0.38 \pm 0.025	6.58
Mineral 1	ND	–	–	ND	–	–	ND	–
Mineral 2	0.15 \pm 0.010	7.14	6.67	0.17 \pm 0.012	21.24	7.06	0.14 \pm 0.010	7.14
Mineral 3	0.21 \pm 0.020	– 8.70	9.52	0.20 \pm 0.021	– 13.04	10.50	0.23 \pm 0.022	9.56
River 1	3.52 \pm 0.220	– 2.22	6.25	3.60 \pm 0.260	0.00	7.22	3.60 \pm 0.210	5.83
River 2	1.25 \pm 0.100	– 8.76	8.00	1.31 \pm 0.120	– 4.38	9.16	1.37 \pm 0.110	8.03
River 3	2.80 \pm 0.230	4.48	8.21	2.75 \pm 0.250	2.61	9.09	2.68 \pm 0.250	9.33
Sea 1	6.67 \pm 0.600	2.61	8.99	6.80 \pm 0.650	4.61	9.56	6.50 \pm 0.50	7.69
Sea 2	12.50 \pm 1.110	5.93	8.88	12.00 \pm 1.100	1.69	9.17	11.80 \pm 0.95	8.05
Sea 3	13.25 \pm 1.250	2.32	9.43	13.60 \pm 1.350	5.02	9.93	12.95 \pm 1.15	8.88

δ^* – relative deviations calculated on the basis of the FAAS reference method.

$$\delta^* = \left[\frac{c_m(PSA) - c_m(FAAS)}{c_m(FAAS)} \right] \cdot 100.$$

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